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ELECTROCHEMISTRY OF SULFUR ADLAYERS ON AG(111).
EVIDENCE FOR A CONCENTRATION- AND POTENTIAL-DEPENDENT SURFACE-
PHASE TRANSITION

by

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13. ABSTRACT (Maximum 200 words) The electrochemical deposition of sulfur adlayers on highly-oriented, thin-film Ag(111) electrodes in aqueous solutions (pH = 13) containing sodium sulfide, Na ₂ S, is reported. Three voltammetric waves, corresponding to the stepwise formation of a sulfur adlayer, are observed at potentials negative of that necessary to induce bulk oxidation of Ag. The total charge obtained by coulometric integration of the three voltammetric surface waves (206 ± 8 μC/cm ²) is equivalent to a sulfur adatom coverage of 1.14 x 10 ⁻⁹ mol/cm ² , in agreement with expectations based on a complete Ag ₂ S _{ads} layer (θ ~ 0.5). The dependencies of the voltammetric response on scan rate and Na ₂ S concentration are used to support a multistep mechanism in which adsorption and oxidation of HS ⁻ yields a nearly complete layer of AgSH _{ads} , prior to a separate and kinetically slow surface-phase transition to an ordered Ag ₂ S _{ads} layer. The voltammetric wave corresponding to the transition of the AgSH _{ads} layer to the ordered Ag ₂ S _{ads} layer is greatly diminished or absent in dilute Na ₂ S solutions, suggesting that a critical sulfur surface concentration is required for the transition to occur. Sulfur desorption studies in solutions containing only supporting electrolyte (no sodium sulfide) also support the conclusion that the surface-phase transition is dependent on the surface concentration of adsorbed sulfur species, as well as the electrode potential.					
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Electrochemistry of Sulfur Adlayers on Ag(111). Evidence for a Concentration- and Potential-Dependent Surface-Phase Transition

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Abstract. The electrochemical deposition of sulfur adlayers on highly-oriented, thin-film Ag(111) electrodes in aqueous solutions (pH = 13) containing sodium sulfide, Na₂S, is reported. Three reversible voltammetric waves corresponding to the stepwise formation of a Ag₂S adlayer, are observed at potentials negative of that necessary to induce bulk oxidation of Ag. The total charge obtained by coulometric integration of the three voltammetric surface waves ($220 \pm 8 \mu\text{C}/\text{cm}^2$) is equivalent to a sulfur adatom coverage of $1.14 \times 10^{-9} \text{ mol}/\text{cm}^2$, in agreement with expectations based on a full Ag₂S layer ($\theta = 0.5$). The dependencies of the voltammetric response on scan rate and Na₂S concentration are used to support a multistep mechanism in which adsorption and oxidation of HS⁻ yields a nearly complete layer of Ag-SH, prior to a separate and kinetically slow surface-phase transition to an ordered Ag₂S adlayer. The voltammetric wave corresponding to the transition of the Ag-SH layer to the ordered Ag₂S layer is greatly diminished or absent in dilute Na₂S solutions, suggesting that a critical sulfur surface concentration is required for the transition to occur. Sulfur desorption studies in solutions containing only supporting electrolyte (no sodium sulfide) also support the conclusion that the surface-phase transition is dependent on the surface concentration of adsorbed sulfur species, as well as the electrode potential.

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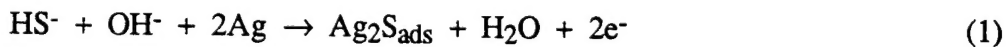
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Introduction. In this paper we describe a voltammetric investigation of adlayers of sulfur on Ag(111) electrodes immersed in aqueous solutions containing HS^- . We demonstrate that the rate of oxidation of the surface bound adsorbate (Ag-SH) to an ordered adlayer structure (Ag_2S) is controlled not only by the electrode potential, but also by the concentration of HS^- in the contacting solution. Our results suggest that a critical surface coverage of adsorbed HS^- is required in order to form the final Ag_2S structure.

It is well established that the structures of atomic adlayers on metal surfaces, synthesized in low-pressure gas environments (by either thermal evaporation or sputtering deposition of foreign atoms onto the metal), may be strongly dependent on the total number of atoms deposited on the surface (i.e., the surface coverage, θ). For instances, at low surface coverage, S atoms deposited in vacuum on tungsten(001) surfaces occupy four-fold hollow sites; at a critical surface coverage corresponding to ca. one half of a full monolayer (i.e., $\theta = 0.5$), a phase transition occurs in which the S adatoms occupy both four-fold hollow and bridging sites.¹ Such observations of concentration-dependent surface-phase transitions in gas-phase environments are relatively common.² In contrast to the experiments performed in low pressure gas-phase environments, electrochemical investigations of adlayer structures in liquid phases have been primarily concerned with the role of the electrode potential in determining the adlayer equilibrium coverage and structure. This experimental focus is largely a consequence of the fact that the number of adatoms (or ions), reversibly adsorbed on a metal surface from the solution phase, is generally a strong function of the magnitude and sign of the electrode potential. Consequently the surface coverage can be varied in a nearly continuous fashion by adjusting the electrode potential versus some suitable reference electrode⁹⁻¹⁰. This capability has largely supplanted other methods of controlling the surface coverage (e.g., changing the concentration of adsorbing species in the solution that are in equilibrium with the surface). Relatively few observations of concentration-dependent adlayer structures have been reported. Hubbard and coworkers, for instance, have shown that the orientation of aromatic molecules

adsorbed onto polycrystalline Pt electrodes can be controlled, independent of the electrode potential, by adjusting the concentration of the molecule in the contacting solution.³

Here we described the step-wise formation of Ag₂S adlayers on Ag(111) electrodes, initiated by the potential-dependent adsorption of HS⁻. The formation of Ag₂S layers on *polycrystalline* Ag has been previously investigated by Horanyi and Vertes⁴, Birss and Wright⁵, Huong et al.⁶, and Hepel et al.⁷ using voltammetric and radiolabeling methods. Although there is disagreement among these researchers on the specific details of the mechanism of adlayer, it is generally accepted that the overall reaction stoichiometry is given by eq. (1) and that the final coverage of Ag₂S_{ads} is ~0.5.



Our experiments on oriented Ag(111) electrodes provide a much more well-resolved separation of the voltammetric waves associated with the intermediate steps of eq. (1), providing evidence that adlayer formation occurs by two, sequential 1-e⁻ oxidations. In addition, in analogy to reports of gas-phase coverage-dependent phase transitions, we demonstrate that structural transition from a Ag-SH adlayer to a ordered Ag₂S layer is dependent on the concentration of the adsorbate in solution contacting the electrode. This latter conclusion is based on non-equilibrium voltammetric measurements, in which the transient adsorbate surface coverage is controlled by slow mass-transport of the adsorbate from the solution to the electrode surface (*vide infra*). We show that approximately one half of a monolayer of Ag-SH is required for the oxidative transition to the final Ag₂S structure.

Experimental.

Sample Preparation. Ag films were epitaxially grown on muscovite mica using an Edwards Auto 306 thermal evaporation system, equipped with a Temescal single head

thickness monitor. Freshly-cleaved mica samples with ($\sim 3 \text{ cm}^2$ area) were placed in a stainless steel substrate holder, positioned $\sim 20 \text{ cm}$ above a resistively-heated Mo boat containing Ag shot (99.9999%). A movable shutter separated the evaporation boat and mica samples. The evaporation chamber was kept at a base pressure of 2×10^{-6} torr using a turbomolecular pump.

Prior to Ag evaporation, the substrate holder and mica were heated to 450°C for 30 minutes to desorb surface impurities. The Mo boat was then resistively heated with the movable shutter in place, allowing Ag to evaporate onto the shutter for 1 minute to outgas impurities in the source. The shutter was opened, and Ag was deposited onto the mica at a rate of 2 \AA/s , until a film thickness of 3500 \AA was obtained. The samples were then annealed at 450°C for 2 hours, cooled to room-temperature under vacuum, and stored under N_2 .

Preparation of Electrodes. The Ag(111) thin-film electrodes were prepared by cutting the Ag-coated mica samples into $\sim 0.4 \times 1 \text{ cm}^2$ rectangles. Copper leads were constructed from flattened 16 gauge wire and attached to the Ag film using a one-part silver epoxy (Dupont 5504N). The electrode was heated in air to 100°C for 3 hours to cure the Ag epoxy. After rinsing the electrodes with reagent-grade methanol, the electrode edges and Cu lead were coated with an inert, high-vacuum silicone grease (Dow-Corning). Electrode areas were $\sim 0.1 \text{ cm}^2$; specific values of electrode areas are listed in the text and figure captions.

Electrochemical cell and Apparatus. A standard one-compartment, three-electrode cell, equipped with ports for inlet and outlet N_2 flow, was used for all experiments. A platinum wire and Ag/AgCl (3M NaCl) electrode were used as the counter and reference electrodes, respectively. Solutions were purged for ~ 20 minutes with N_2 before each measurement to

remove O₂ from the solution. A steady stream of N₂ was passed over the solution during measurements. Measurements were made at $25 \pm 2^\circ\text{C}$.

Voltammetric data were obtained using a Princeton Applied Research Corp. (PARC) Model 173 Potentiostat and a Model 175 Universal Programmer. A Kipp and Zonen Model BD-90 x-y recorder was used to record voltammetric curves.

Chemicals. All solutions were prepared using water obtained from a Barnstead "E-pure" water purification system. PbO (Fischer), NaOH (Mallinckrodt), HCl (Mallinckrodt) and Na₂S (Mallinckrodt) were reagent grade, and used as received.

Results and Discussion.

Characterization of the Ag(111) electrode. Glancing angle x-ray crystallography was used to determine the orientation of the evaporated films. Fig. 1 shows a typical diffraction pattern obtained for a 3500 Å-thick film, along with the 2θ values expected for diffraction from different surface orientations. In agreement with the expected epitaxially growth of Ag (111) on mica,⁸ the diffraction pattern exhibits strongest intensities for the (111) and (222) indices. The relative intensity corresponding to the (200) reflection is very small and that for the (220) orientation is not present. The results indicate that the film electrodes have a predominantly (111) orientation (> 85%).

The underpotential deposition (upd) of a Pb monolayer on the Ag thin-film electrodes was also examined to confirm the (111) orientation. The voltammetric response for the upd of Pb on Ag displays unique response features for each of the 3 low-index orientations of Ag, as has been previously determined from studies using single crystal electrodes.⁹ Thus, the voltammetric response can be used to evaluate the surface orientation. Fig. 2 shows the voltammetric response for the evaporated Ag film in a 0.5 M HClO₄ solution containing 5 mM PbO. The sharp wave (FWHM = 7.5 mV) centered at -0.295 V vs Ag/AgCl corresponds to the upd deposition of one Pb monolayer on a

Ag(111) surface, in excellent agreement with the voltammetric response reported by Bewick and Thomas⁷ using single crystal Ag(111) electrodes (for comparison, upd of Pb on the (110) and (100) orientations results in multiple and broader waves at different electrode potentials relative to that observed for the (111) surface). The coulometric charge associated with the upd process, obtained by integration of the cathodic stripping peak in Fig. 2, is $324 \mu\text{C}/\text{cm}^2$, in good agreement with the theoretical value of $302 \mu\text{C}/\text{cm}^2$ expected assuming a close pack Pb monolayer (using 1.75\AA for Pb radius). Our measured value is also agrees with the value $(334 \pm 4 \mu\text{C}/\text{cm}^2)$ measured by Bewick et al.⁷

Voltammetry of Ag(111) in Na₂S Solutions.

The steady-state voltammetric response of the Ag(111) thin-film electrode in solution containing 0.75 mM Na₂S and 0.2 M NaOH is presented in Fig. 3a. For this solution composition (as well as all others reported herein), the primary S species present in the solution is hydrosulfide, HS⁻ (>99.99 %), as determined from the literature pK_a values for H₂S (7.02) and HS⁻ (17.1).¹⁰

Three well-resolved surface waves are present in the voltammetric response with half-wave potentials, $E_{1/2}$, of -1.20V, -1.05V, and -0.88 V vs. Ag/AgCl (where $E_{1/2} = (E_{pc} + E_{pa})/2$, and E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively). We will refer to these waves as A, B, and C, respectively, as indicated in Fig. 3. Voltammetric curves obtained in solutions containing only 0.2 M NaOH (dashed line in Fig. 3a) show a featureless capacitive current.

The bulk oxidation of the Ag film, resulting in the formation of a thick Ag₂S layer begins at ~ -0.69 V vs Ag/AgCl. Repeated cycling of the electrode potential into the region where bulk oxidation occurs is reported to lead to roughening of polycrystalline electrodes. In order to prevent surface roughening, a positive potential limit of ~ -0.76 V was used in all of our voltammetric experiments.

We intentionally spiked the Na_2S solutions with 0.05 mM NaCl to determine if any of the 3 surface waves was influenced by the adsorption of impurity Cl^- , potentially introduced into the solution at the Ag/AgCl reference electrode/electrolyte junction. The voltammetric response shown in Fig. 3a was unaffected by the intentional addition of Cl^- .

Before describing the surface chemistry leading to the observed voltammetric response shown in Fig. 3a, we note that a somewhat similar voltammetric response is obtained for polycrystalline Ag electrodes. Fig 3b shows the steady-state voltammetric curve for a polycrystalline Ag wire, obtained in the same solution used to record the voltammetric wave of the thin-film (111) electrode. A similar 3-wave response is observed prior to bulk oxidation of the Ag , with anodic peaks A, B and C occurring at $E_{1/2} = -1.21, -1.12, \text{ and } -0.90\text{V}$, respectively. An essentially identical response to that shown in Fig. 3b was reported by Hepel et al.⁶ using a rotating polycrystalline Ag disk electrode immersed in a HS^- solution. These researchers attributed the 3-wave pattern to the "three distinct surface processes with differences in the sulfur adsorption energy at three kinds of sites on the silver surface, possibly different crystallographic orientations." This conclusion suggests that a single voltammetric wave should be observed on a single crystal or highly oriented Ag (111) electrode. Our observation that the surface processes on oriented $\text{Ag}(111)$ surface results in a similar 3-wave response strongly suggests that Hepel et al.'s interpretation based on energetically-different adsorption on different orientations is at least partially incorrect. To determine if surface restructuring of our electrodes occurred during voltammetric experiments in Na_2S solutions, the upd of Pb on an Ag electrode was examined prior to and after repeated potential cycling in a Na_2S solution. The upd response (including the initial scan) was found to be identical before and after cycling in Na_2S solution, indicating that surface restructuring is insignificant.

Birss and Wright and Horanyi and Vertes³⁻⁴ have performed voltammetric studies of Ag_2S adlayer formation on polycrystalline Ag in basic solutions. Both groups reported a single voltammetric wave at $\sim -0.9\text{ V}$ vs Ag/AgCl , which clearly corresponds to wave C

in our studies (Fig. 3a and b). Interestingly, neither of these groups reported observing waves A or B, for reasons that are not entirely clear. However, using ^{35}S labeled Na_2S and radiotracer techniques methods, Horanyi and Vertes demonstrated that adsorption (and possible oxidation) of HS^- begins at potentials -0.5 negative of wave C, well within the voltage range (-1.3 to -1.0) encompassing waves A and B. Based on this evidence, Horanyi and Vertes⁴ concluded that the formation of the Ag_2S adlayer proceeds by (at least) two separate oxidative steps at different potentials, represented by eqs. (2) and (3). Birss and Wright⁵ also suggested a similar multistep process, with slow charge transfer from the surface adsorbate HS^- (eq. (2)) being the rate determining step.



In addition, based on an analysis of the dependence of the shape of wave C on scan rate and Na_2S concentration, Birss and Wright proposed that eq. (3) proceeds by a two-dimensional nucleation and growth process, involving surface diffusion of adsorbed SH .⁵ As shown in the following sections, our results using oriented $\text{Ag}(111)$ strongly support the conclusion that adlayer formation occurs by sequential oxidations at two different potentials, with wave A and B corresponding to the oxidative adsorption of HS^- (eq. (2)) and wave C corresponding to oxidation of AgSH_{ads} (eq. (3)). In addition, we also show that a critical coverage of AgSH_{ads} is required in order for eq. (3) to proceed at measurable rates, supporting the hypothesis that wave C corresponds to a relatively slow phase-transition.

Scan Rate Dependence and Coverage. Fig. 4 shows the dependence of the voltammetric response on scan rate, v . The shape of waves A and B remain relatively constant with

increasing scan rate, with a small increase (~ 10 mV) in the separation between the anodic and cathodic peak potentials (E_{pc} and E_{pa}) of each wave. On the other hand, the peak splitting ($E_{pa} - E_{pc}$) for wave C is relatively significant, increasing from 15 mV at 5 mV/s to 55 mV at 100 mV/s. The FWHM of either the cathodic or anodic peak of wave C also decreases significantly at slower scan rates, obtaining a value of ~ 7 mV at the slowest scan rate employed (5 mV/s).

The dependence of the anodic peak current, i_p , on scan rate ($5 \leq v \leq 200$ mV/s) for all three waves is plotted in Fig. 5, which shows that i_p is proportional to v for waves A and B, but has a nonlinear dependence on v for wave C. The linear dependence of i_p on scan rate and symmetrical shape of waves A and B suggest that these two waves are associated with surface processes that are relatively fast and reversible on the voltammetric time scale. We associate these two waves with the oxidative adsorption of HS^- (eq. (2)), in agreement with the conclusion of Horanyi and Vertes based on radiolabeling methods. The appearance of two waves (A and B) suggest that the adsorption is more complex than is indicated in eq. (2), perhaps involving cation coadsorption and/or potential dependent structural rearrangement of the adlayer. Our present data does not allow a more detailed assignment of these subtle processes.

In Fig. 6, we show that the anodic peak current, i_p , for wave C is proportional to the scan rate raised to the $2/3$ power, $v^{2/3}$. The $2/3$ -power dependence is consistent with models of voltammetric processes associated with 2-D phase-transitions and/or film growth¹¹. This finding strongly suggests that wave C is associated with the oxidative phase transition eq. (3), from a $AgSH_{ads}$ structure to an ordered Ag_2S layer. The inset of Fig. 6 shows that a plot of i_p vs the square root of the scan rate, $v^{1/2}$, is not linear, eliminating the possibility of wave C arising from diffusion-limited transport of HS^- from solution.

The assignments of waves A and B to eq. (2) and wave C to eq. (3) allow semi-quantitative predictions of the coulometric charge, Q , associated with each wave, since the

number of electrons ($n = 1$) in each reaction is predicted by eqs. (2) and (3). Integration of the area under waves A + B (combined) and that for wave C, shows that an equivalent amount of charge ($Q \sim 110 \mu\text{C}/\text{cm}^2$) is associated with eqs. (2) and (3), consistent with $n = 1$ for both reactions. In 0.5 mM Na_2S solutions, we find that charge associated with these processes is independent of scan rate (between 5 and 200 mV/s).

The total charge computed from the area under voltammetric waves A, B, and C is $220 \pm 8 \mu\text{C}/\text{cm}^2$. Assuming a complete adlayer of Ag_2S (i.e., 1 S atom per 2 Ag atoms) and $n = 2$, and using the surface atom density for Ag(111), 1.387×10^{15} atoms/ cm^2 , the theoretical charge density expected for adlayer formation is $222 \mu\text{C}/\text{cm}^2$. The agreement between measured and theoretical charge densities supports our assignment of the voltammetric waves to discrete oxidation reactions (eqs. (2) and (3)).

It is interesting to note that the 3-wave voltammetric response that for Ag_2S adlayer formation is quite similar to that for halide and SO_4^{2-} adsorption on Au and Ag single-crystal electrodes¹²⁻¹⁷. Although the details of the voltammetric responses for each of these anion adsorption systems are somewhat different, a common feature of each is the appearance of a rather broad, reversible wave(s), separated from a much sharper peak at a more positive potential. Recent in-situ scanning tunneling microscopy and X-ray studies show that the sharp peak, at the more positive electrode potential, is due to small increase in the surface coverage concurrent with a structural ordering of the adlayer.^{11,12,13} The broader wave at negative potentials is reported to be due to reversible anion adsorption (and oxidation). The three-wave pattern we observe for sulfur on Ag has the same general appearance as the voltammetric pattern of these other systems; however, the coulometric charge associated with the adlayer transition (wave C) is considerably larger in our case. For example, for I^- adsorption on single-crystal Au electrodes, the coulometric charge associated with an adlayer phase transition is only a few percent of that associated with the initial adsorption process. In comparison, we observe that the charge associated with wave C ($\sim 110 \mu\text{C}/\text{cm}^2$) is essentially equivalent to that of adsorption waves (A and B

summed together). This difference is rationalized by noting that, for the Ag_2S system, an additional electron-transfer and proton-loss step (eq. 3) occurs at the same electrode potential as the phase transition. Thus, an approximately equal coulometric charge is expected for adsorption (waves A plus B) and phase transition (wave C) in the present case. It does not seem altogether surprising that the electron-transfer step and structural phase-transition occur simultaneously, since oxidation of the $\text{Ag-HS}_{\text{ads}}$ leads to a significant change in the chemical bonding and, thus, atomic arrangement, within the adlayer. In the following sections, we present evidence that a critical surface concentration of $\text{Ag-HS}_{\text{ads}}$ is required for this oxidative phase-transition to occur.

Desorption of Ag_2S Adlayers

Desorption of the Ag_2S adlayer was studied in solutions containing only NaOH (0.2 M). To perform these investigations, a $\text{Ag}(111)$ electrode coated with a complete Ag_2S adlayer was prepared by scanning the electrode potential between -1.33V to -0.76V in a solution containing both 0.5 mM Na_2S and 0.2 M NaOH . The response observed in this solution is shown at the bottom of Fig. 7, and is essentially identical to that in Fig. 3a. The electrode was then removed from the Na_2S solution *under potential control* at -0.76V (slightly positive of wave C) and immediately immersed in a solution containing only 0.2M NaOH . Removal of the electrode from the Na_2S solution at -0.76 V ensures that a complete layer of Ag_2S is formed on the surface prior to the desorption studies.

Fig. 7a shows the voltammetric response over a potential range encompassing only wave C. On the first scan, beginning at -0.76 V, a relatively large cathodic peak is observed that corresponds to the reduction of Ag_2S to adsorbed HS. The magnitude of this wave is essentially identical to that of wave C in the steady-state response (see bottom of Fig. 7). On the reverse (positive-going) scan, the anodic peak corresponding to the oxidation of adsorbed HS is greatly reduced, suggesting that HS rapidly desorbs from the electrode surface. Repetitive cycling of the electrode over this range results in complete

loss of electrochemical activity. Wave C is not recovered by holding the potential for extended periods at either the positive or negative limits of the voltammetric scan.

The positive and negative potential limits in the voltammetric experiment were then shifted to negative values such that waves B and A were individually examined in the NaOH solution (Fig. 8b and 8c). The first scan in each of these sets of voltammograms shows a cathodic wave with peak heights slightly smaller relative to those observed in the steady-state response. *This finding clearly suggests that desorption of HS does not occur to a large extent during voltammetric cycling over wave C, as is suggested by the rapid diminishment of that wave in the initial part of the experiment (Fig. 7a).* Rather, we propose that loss of electrochemical activity associated with wave C is a consequence of the Ag-HS to Ag₂S surface transition (eq. (3)) requiring not only a sufficiently positive electrode potential to occur, but also a critical surface coverage of HS. Undoubtedly, there is some small and irreversible loss of sulfur species from the surface when cycling the electrode potential around wave C in solutions not containing HS⁻. Our findings suggest that this loss is rather small (< 5%), as indicated by the fact that waves B and A (Fig. 7b and 7(c)) have similar peak heights as in a solution containing HS⁻ (Fig. 7(c)). However, the loss is sufficiently large that the phase transition is no longer energetically favorable or becomes immeasurably slow on the voltammetric timescale. As noted in the *Introduction* section, the notion of a critical surface coverages being required to induce a surface phase transitions is relatively common in vacuum studies of adlayer structures. The coverage dependence of adlayer transitions in electrochemical studies, however, is generally expressed only as an implicit function of the electrode potential, rather than as an independent factor. Our ability to observe the disappearance of the voltammetric response associated with a surface transition (i.e., wave C), while being able to quantitatively monitor the surface coverage through the adsorption/desorption process (wave A and B) demonstrates that both electrode potential and surface coverage can be independently controlled.

Dependence on Na₂S Concentration.

The above ideas suggest that the voltammetric response of a Ag(111) electrode should be a function of the dissolved HS⁻ concentration, if sufficiently dilute HS⁻ solutions could be prepared such the potential-dependent surface coverage of S species, θ , could be maintained at a value lower than the potential-dependent saturation surface coverage, θ_{sat} . Here, θ_{sat} is defined as the coverage observed in solutions in which the HS⁻ concentration is sufficiently large that the maximum surface coverage is attained on the experimental time scale. The attainment of an equilibrium surface coverage requires that the rate of transport of HS⁻ to the surface is fast on the voltammetric time scale. For example, the observed linear dependence of peak currents on scan rate for waves A and B, Fig. 5, clearly demonstrates that eq. (2) is not limited by diffusion of HS⁻. However, diffusion of HS⁻ to the surface can become rate limiting if the solution concentration of HS⁻ is sufficiently small.

Fig. 8 shows the steady-state voltammetric response of a Ag(111) electrode as a function of the concentration of Na₂S dissolved in the solution (0.2 M NaOH). The interesting feature of this set of data is that wave C is strongly dependent of the Na₂S concentration, decreasing rapidly for [Na₂S] < 0.3 mM, and vanishing altogether at [Na₂S] ~ 0.05 mM. The voltammetric response for wave A remains relatively constant over the same concentration range, diminishing only slightly with decreasing [Na₂S].

The dependence of the voltammetric response on [Na₂S] is due to slow diffusion of HS⁻ in the solution to the electrode surface, preventing the attainment of an equilibrium saturation coverage of sulfur at any potential. To demonstrate this, we performed an experiment in which the potential scan was stopped at the positive potential limit (~ -0.76 V), and held there for 60 s before scanning towards negative potentials. The measurements were made in a solution containing Na₂S at a concentration sufficiently low that wave C was completely absent in the steady-state response, Fig 9(a). As shown by Fig. 9(b), the

effect of pausing the voltammetric scan for 60 s is to cause the cathodic peak for wave C to reappear, with an magnitude comparable to that obtained in a much more highly concentrated Na_2S solution. The reappearance of the peak C clearly results from the fact that the surface coverage of $\text{Ag}_2\text{S}_{\text{ads}}$ increased during the pause in the voltammetric sweep.

In Fig. 10 we plot the charge densities computed from the integrated areas of waves A and B (summed together) and wave C as a function of the Na_2S concentration. We find that the charge corresponding to wave C decreases to negligible value at much higher concentrations of Na_2S than does the charge associated with waves A and B. As in the desorption studies, we interpret this finding as evidence of the requirement of a critical coverage of AgSH_{ads} prior to the phase transition to $\text{Ag}_2\text{S}_{\text{ads}}$. It is interesting to note that the coulometric charge associated with the formation of $\text{Ag}_2\text{S}_{\text{ads}}$ has a non-zero value only when that for AgSH_{ads} reaches $\sim 50\%$ of its apparent saturation value. This finding clearly suggests that a relatively high coverage of AgSH_{ads} is required ($\theta \sim 0.25$) prior to formation of the final $\text{Ag}_2\text{S}_{\text{ads}}$ structure.

Conclusion. The electrochemical formation of Ag_2S adlayers on $\text{Ag}(111)$ has been shown to occur by a multistep process involving the intermediate AgSH_{ads} , consistent with earlier mechanisms proposed by Birss and Wright⁵ and Horanyi and Vertes⁴. In addition, our voltammetric studies indicate the electrochemical oxidation of AgSH_{ads} to $\text{Ag}_2\text{S}_{\text{ads}}$ is strongly dependent on the absolute surface coverage of AgSH_{ads} , as well as the electrode potential. As previously noted, coverage-dependent transitions are frequently observed in high-vacuum studies of interfacial structures, and are generally interpreted as a means whereby lateral repulsive forces within the film are reduced. Our results suggest that the formation of the $\text{Ag}_2\text{S}_{\text{ads}}$ structure is energetically favorable only when there is a strong lateral interaction within the adlayer (i.e., at high coverages).

The strong dependence of the oxidative phase transition on the surface coverage raises the issue of whether the electron-transfer step (eq. (3)) is a consequence of

adsorbate-adsorbate interactions. Precedent for this suggestion comes from high vacuum studies, in which the degree of charge transfer between a metal surface and alkali adatoms has been shown to decrease with increasing alkali surface coverage, a consequence of in-plane electrostatic forces between neighboring adatoms.¹⁸ Similar lateral interactions at high coverages, e.g., dipole-dipole interactions between adsorbed SH, may induce (in addition to the normal interfacial fields) the observed electron-transfer reaction and phase transition in S adlayers. Although we are not aware of a similar surface-coverage dependence in other electrochemical systems, there have been few investigations in which the roles of the surface coverage and electrode potential have been cleanly separated, as has been partially accomplished in the present paper. Whether this phenomenon is as common in electrochemical systems as in high vacuum systems requires more systematic studies, as well as the use of experimental methods that allow the coverage and potential dependencies to be separately revealed.

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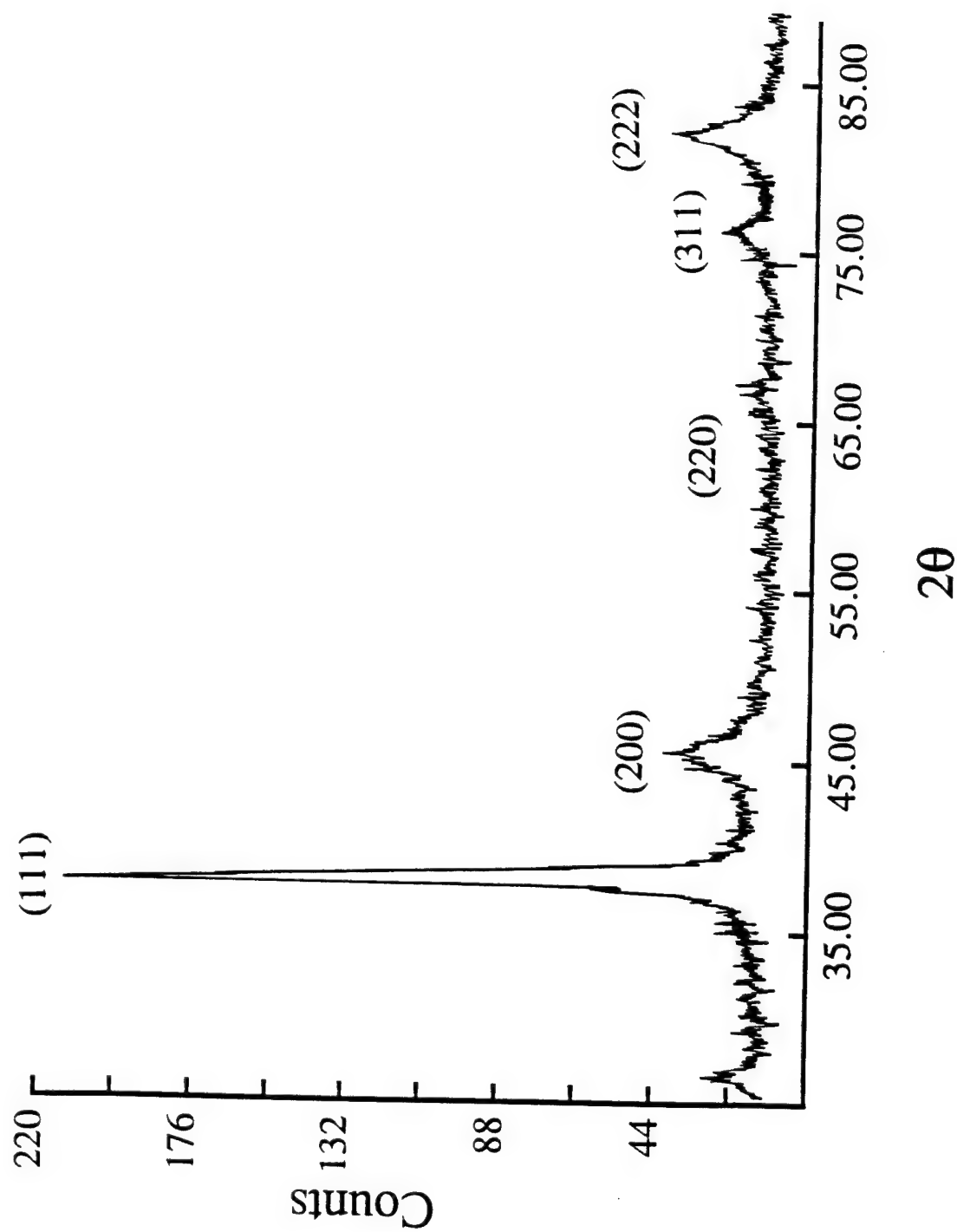
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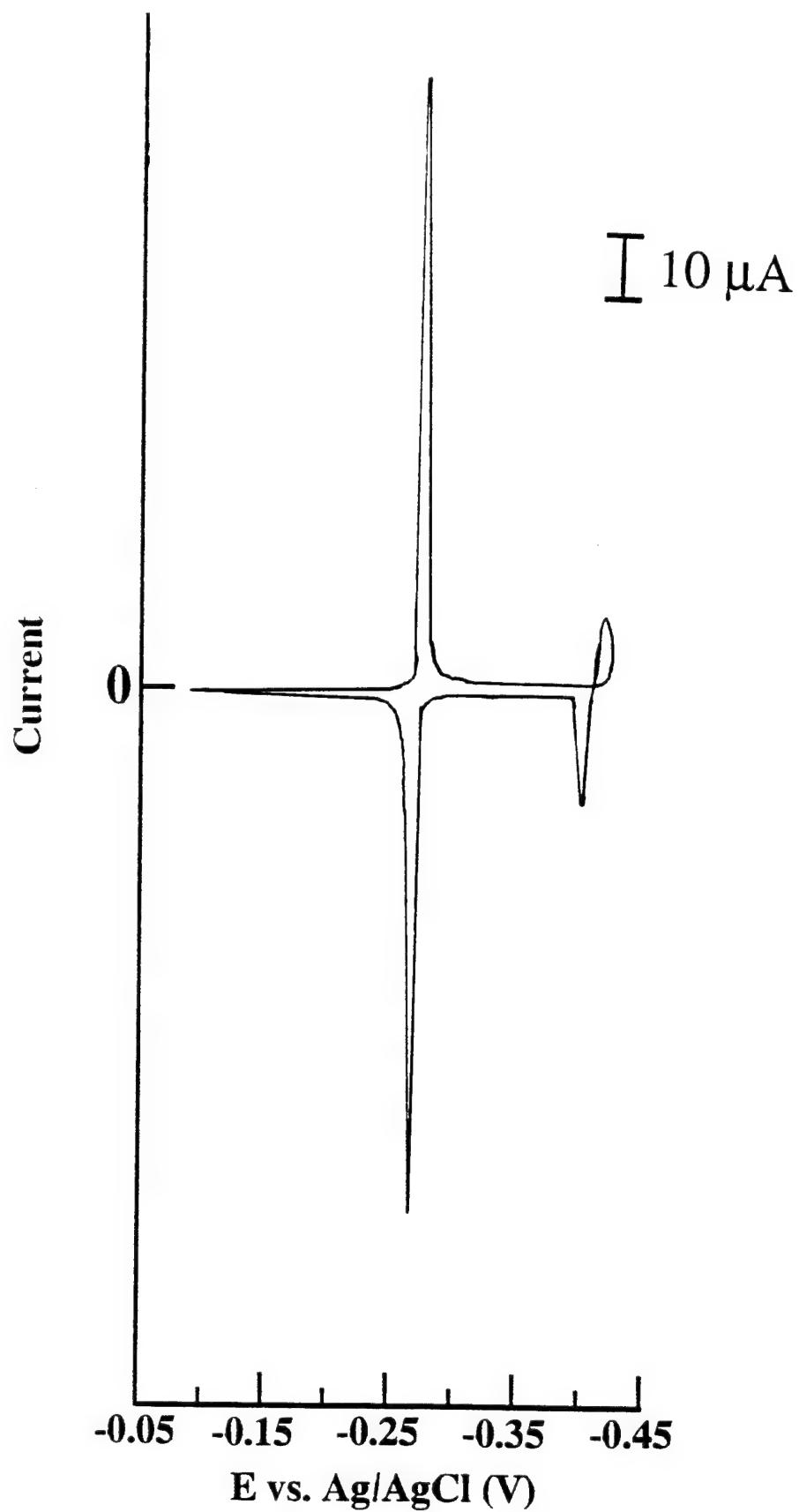
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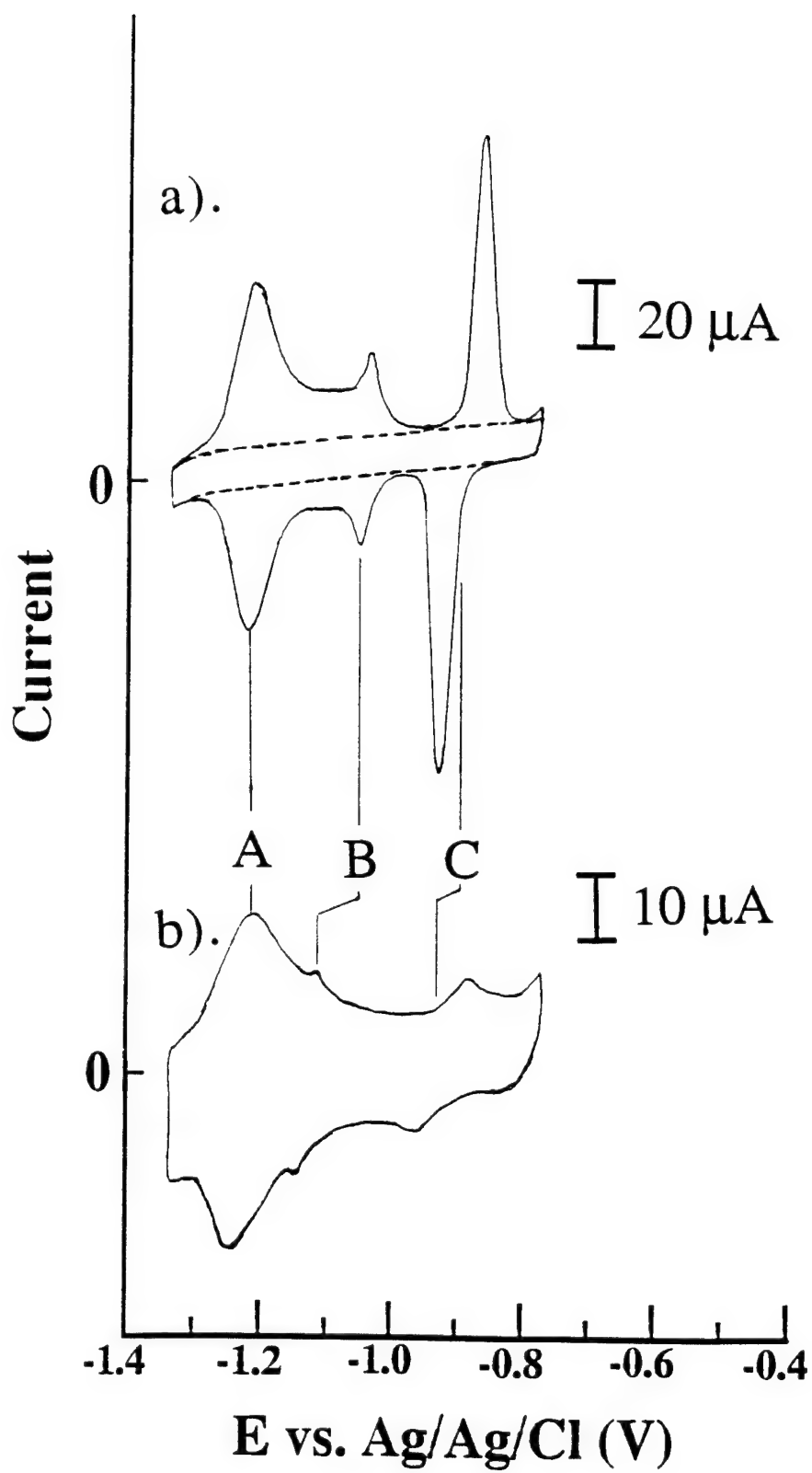
Figure Captions

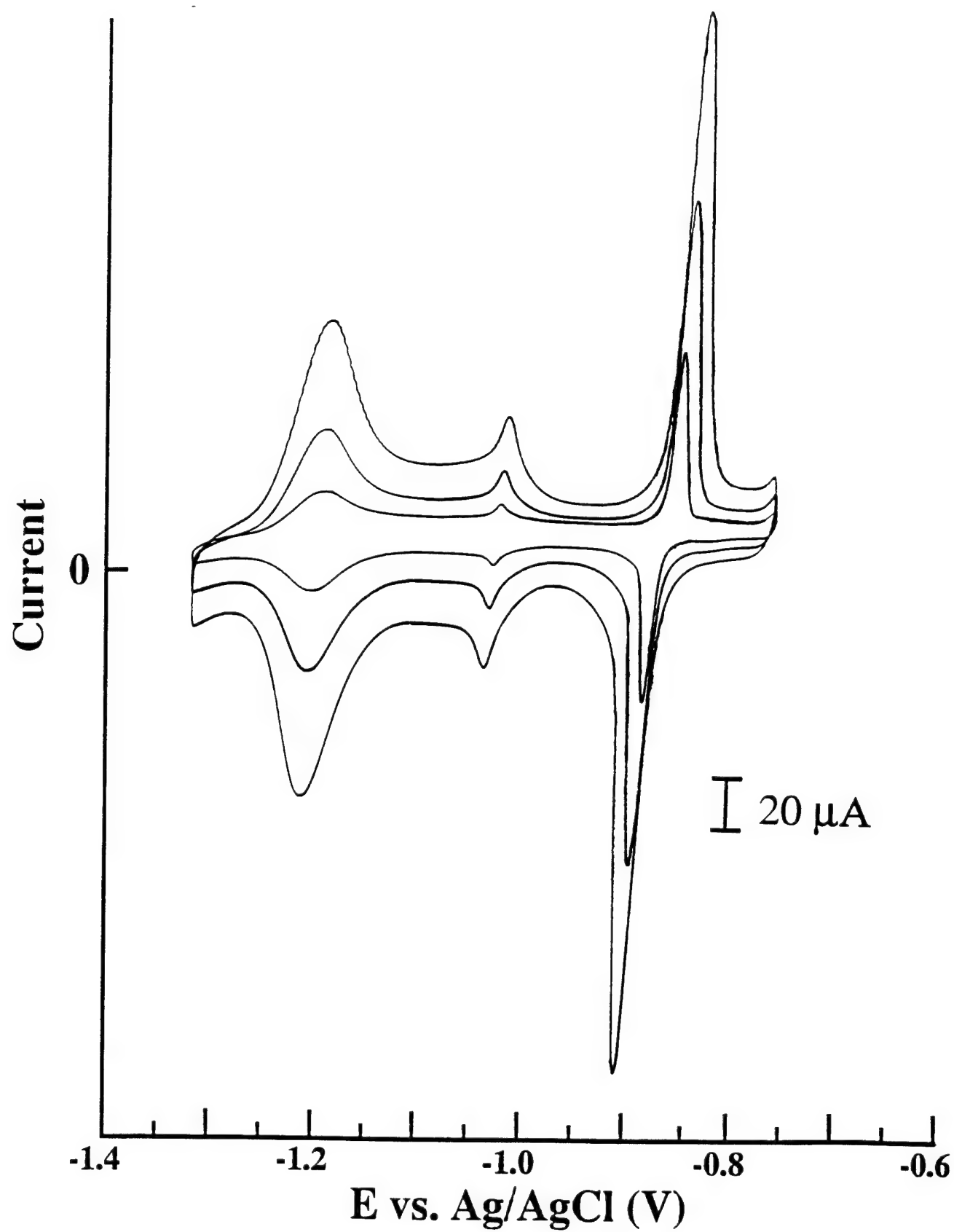
1. Glancing angle diffraction pattern for a 3500 Å-thick Ag film on mica.
2. Voltammetric response of a Ag(111), thin-film electrode in a N₂-purged, 0.5 M HClO₄ solution containing 5 mM PbO. Scan rate: 30 mV/s. The area under the cathodic peak corresponds to a charge density of 324 μC/cm².
3. Voltammetric response of (a) Ag(111) thin-film electrode and (b) polycrystalline Ag wire in a N₂-purged, 0.2 M NaOH solution containing 0.5 mM Na₂S. Scan rate: 100 mV/s. The dashed line in (a) corresponds to the voltammetric response in a 0.2 M NaOH solution (no Na₂S).
4. Scan-rate dependence of the voltammetric response of a Ag(111) thin-film electrode in a N₂-purged, 0.2 M NaOH solution containing 0.5 mM Na₂S. Scan rates: 20, 50 and 100 mV/s. Electrode area: 0.15 cm².
5. Anodic peak currents for waves A, B, and C as a function of scan rate. Same solution as described in Fig. 4.
6. Anodic peak current for wave C plotted versus (scan rate)^{2/3}. Inset: peak current vs. (scan rate)^{1/2}. Same solution as described in Fig. 4.
7. Voltammetric response of Ag(111) electrode in a blank 0.2 M NaOH solution (no Na₂S) showing the sequential potential-dependent desorption of the Ag₂S adlayer. (a) Initial voltammetric scans between -.76 and -.98 V showing the disappearance of wave C; (b) voltammetric scan between -.76 and -1.10 showing the disappearance of wave B; (c) voltammetric scan between -.76 and -1.33 V showing the disappearance of wave A. (d) steady-state response of the Ag(111) electrode in a 0.2 M NaOH, 0.5 mM Na₂S solution prior to desorption experiments.

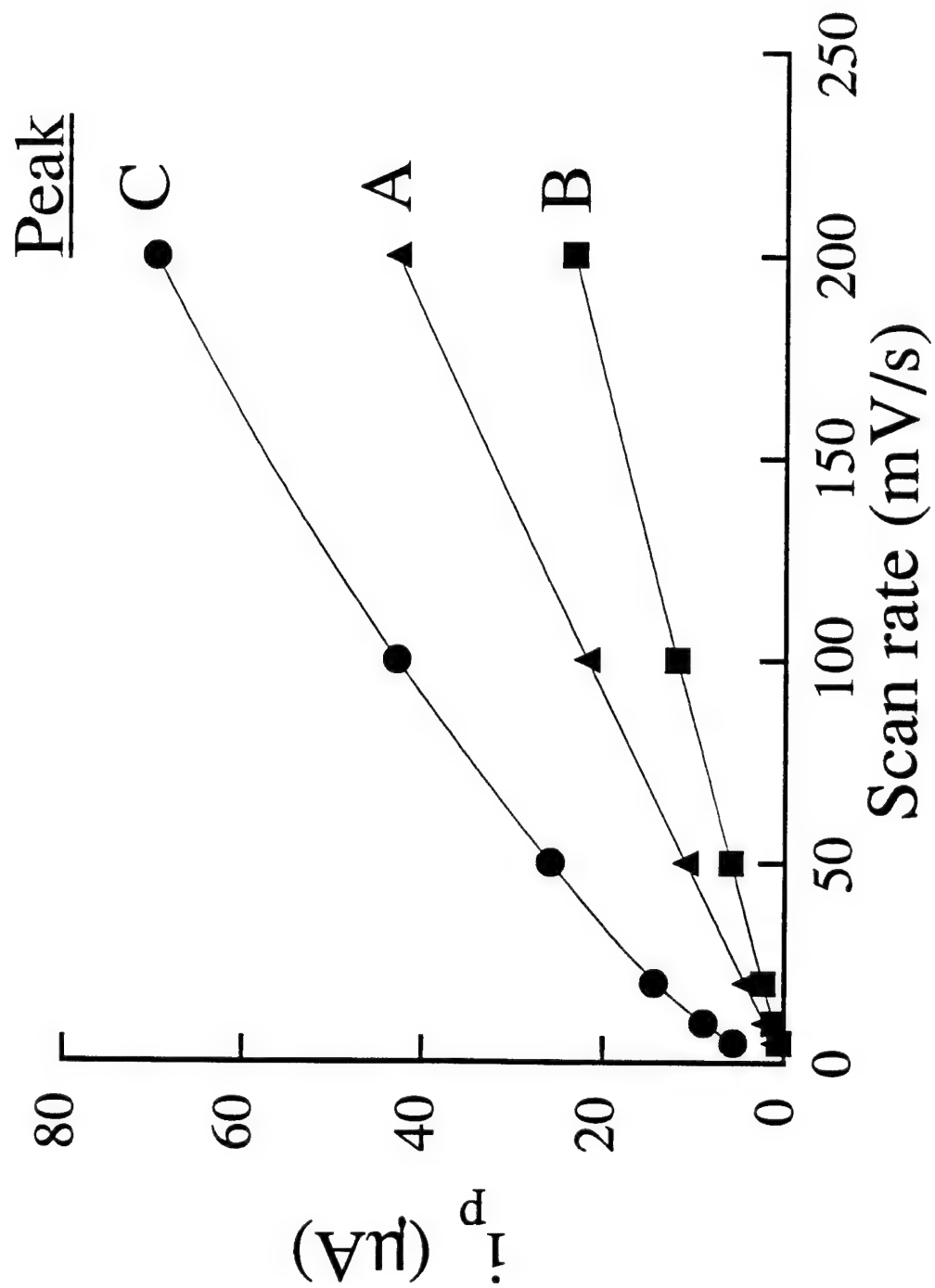
8. Steady-state voltammetric response of a Ag(111) thin-film electrode in a N₂-purged, 0.2 M NaOH solution as a function of Na₂S concentration. Scan rate: 100 mV/s.
9. (a) Steady-state voltammetric response of a Ag(111) thin-film electrode in a N₂-purged, 0.2 M NaOH solution containing 5.0×10^{-5} mM Na₂S. (b) Same as in (a) except that the potential sweep is paused at the positive limit (-.76 V) for 60 s. Scan rate: 100 mV/s.
10. Surface charge density obtained by integration of voltammetric waves A and B (open circles) and wave C (filled circle) as a function of Na₂S concentration. All measurements made in a N₂-purged solutions containing 0.2 M NaOH at a scan rate of 100 mV/s.

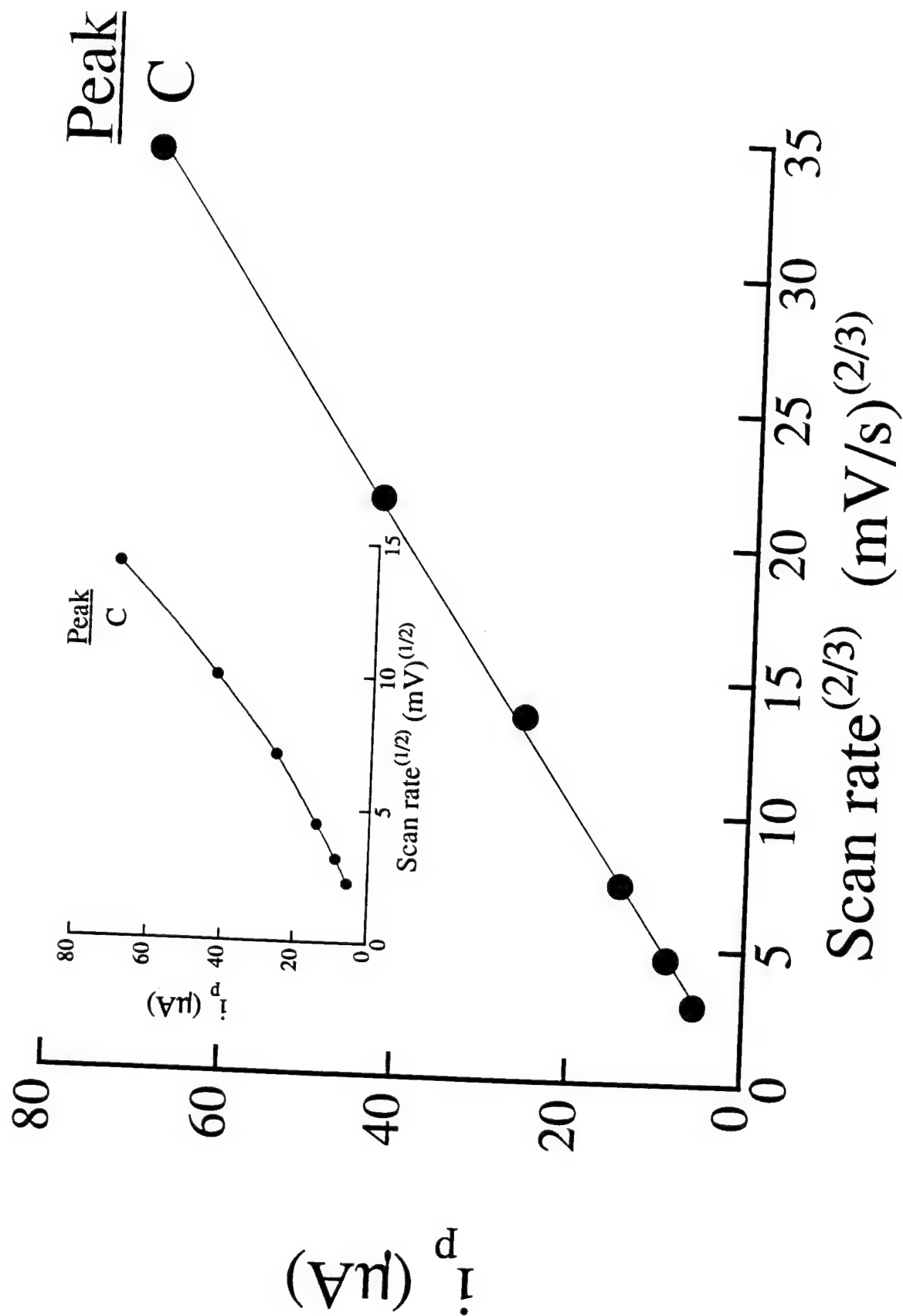


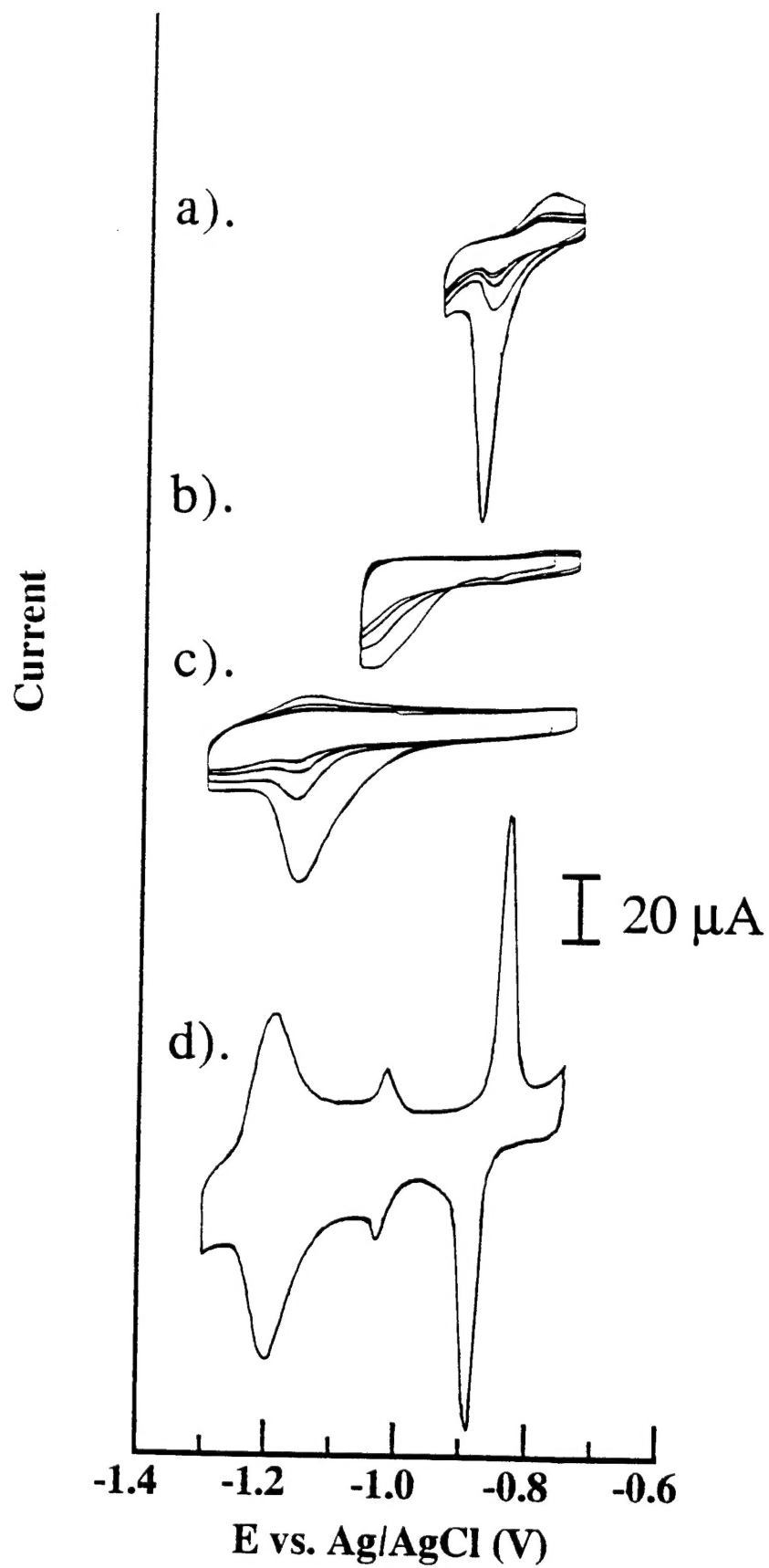












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